



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification</b> : <b>C09K 7/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/34963</b> <b>(43) International Publication Date:</b> 25 September 1997 (25.09.97)
<b>(21) International Application Number:</b> PCT/US97/04611 <b>(22) International Filing Date:</b> 20 March 1997 (20.03.97)  <b>(30) Priority Data:</b> 08/620,983      22 March 1996 (22.03.96)      US  <b>(71) Applicant:</b> EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US).  <b>(72) Inventors:</b> WITTENBRINK, Robert, J.; 836 Shadyglen Drive, Baton Rouge, LA 70816 (US). MART, Charles, J.; 457 Dakota Lane, Coppell, TX 75019 (US). RYAN, Daniel, F.; 6211 Gabriel Oaks Drive, Baton Rouge, LA 70820 (US).  <b>(74) Agents:</b> SIMON, Jay et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).		<b>(81) Designated States:</b> AU, CA, JP, MX, NO, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> HIGH PERFORMANCE ENVIRONMENTALLY FRIENDLY DRILLING FLUIDS  <b>(57) Abstract</b>  The invention discloses an environmentally friendly drilling fluid, or mud, composition useful in the production of oil and gas. The drilling fluid is constituted of one or more of weighting agents, emulsifiers, wetting agents, viscosifiers, fluid loss control agents, proppants, and other particulates such as used in a gravel pack, emulsified with a paraffinic solvent composition which forms a continuous oil phase, or water-in-oil invert phase. The solvent composition is constituted of a mixture of C <sub>10</sub> -C <sub>24</sub> n-paraffins and isoparaffins having an isoparaffin:n-paraffin molar ratio ranging from about 0.5:1 to about 9:1, and the isoparaffins of the mixture contains greater than 50 percent of mono-methyl species, based on the total weight of the isoparaffins in the mixture.		

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## HIGH PERFORMANCE ENVIRONMENTALLY FRIENDLY DRILLING FLUIDS

### Related Application

This is a continuation-in-part of Application Serial No. 569,466 filed December 8, 1995.

### 1. Field of the Invention

This invention relates to substantially non-toxic, non-polluting, biodegradable wellbore, or drilling fluid compositions, or muds, useful in the production of oil and gas. In particular, it relates to improved drilling fluid compositions of this character which possess rheological properties useful as wellbore fluids.

### 2. Background

In rotary drilling, completion and workover operations for the production of oil or gas, in normal circulation, drilling fluid, or mud, is pumped downwardly through a rotating drill string to the bit at the bottom of the wellbore and returned to the surface through the annulus; or, in reverse circulation, downwardly through the annulus and returned through the drill string. It is essential, in these operations to condition or maintain the mud at a proper gel strength, viscosity, density, etc. by the use of additives, the removal of sand and other solids, the removal of gas, the addition of a liquid, e.g., water or hydrocarbon, and other measures to prepare the mud for a wide range of conditions encountered in the well.

Several important functions are served by the drilling fluid, or mud, to wit: clean the bit and bottom of the borehole so that the bit can drill; remove and transport drill cuttings to the surface; cool and lubricate the bit and drill string; maintain pressure balance between the geological formations and the wellbore; seal permeable formations; and provide, with routine testing of the mud, information about the formation penetrated.

Various materials are added to prepare and condition drilling muds. A principal component of a drilling fluid, or mud, is a weighting additive, generally pulverized barite.

Other additives include, besides the weighting agent, emulsifiers, wetting agents, viscosifiers, fluid loss control agents, particulate agents for forming a gravel pack, and proppants for use in hydraulically fracturing subterranean formations, e.g., ground nut hulls, cellophane, etc.

Oil base drilling fluids provide many advantages over water base drilling fluids because of their excellent lubricating characteristics. Most are based upon mineral oils or diesel oil with the addition of additives therein to effect an emulsion in which the oil provides a continuous phase. However, the pollution and toxic features produced by the use of mineral oils or diesel oil have become increasingly objectionable because the oils tend to escape into the environment, contaminating both the land and the water. Spent drilling fluids and drilling cuttings are thus among the most significant waste streams from oil explorations, and pose a serious and costly disposal problem for operators, especially off-shore operators who must barge spent mud and cuttings to shore for land disposal if the materials do not meet EPA discharge limitations or permit requirements. For this reason, considerable effort has been made to avoid the use of muds which contain mineral oils and diesel oils; and more recently, efforts have been made to use materials other than these to produce non-polluting, non-toxic, biodegradable-drilling fluids, or muds with good rheological properties. There exists a need for muds of this character, particularly more environmentally friendly muds which retain the high lubricating characteristics of the more conventional oil base drilling fluids, or muds.

### 3. Summary of the Invention

This invention, which supplies this and other needs, accordingly relates to a substantially non-toxic, essentially non-polluting, biodegradable drilling fluid, or mud, composition comprised of a continuous oil phase, or water-in-oil invert emulsion phase, of a mixture of normal paraffins (n-paraffins) and isoparaffins having from about 10 to about 24 carbon atoms, i.e., C<sub>10</sub>-C<sub>24</sub> n-paraffins and isoparaffins, preferably C<sub>12</sub>-C<sub>18</sub> paraffins, having an isoparaffin:n-paraffins molar ratio ranging from about 0.5:1 to about 9:1, preferably from

about 1:1 to about 4:1, and the isoparaffins of the mixture contain greater than 50 percent preferably greater than 70 percent, based on the total weight of the isoparaffins in the mixture, of mono-methyl species, e.g., 2-methyl, 3-methyl, 4-methyl,  $\geq 5$ -methyl or the like, with minimum formation of branches with substituent groups of carbon number greater than 1, e.g., ethyl, propyl, butyl or the like. The paraffinic solvent mixture boils within a range of from about 320°F to about 700°F, preferably within a range of from about 500°F to about 700°F. The most preferred portion of the solvent mixture boils within a range of from about 500°F to about 550°F.

The  $C_{10}$ - $C_{24}$ , or  $C_{12}$ - $C_{18}$  solvent composition of the drilling fluid, or mud, in all embodiments constitutes a continuous liquid phase, or continuous invert emulsion phase where water or brine is present and emulsified within the solvent composition. Where water is present, the solvent:water volume ratio generally ranges from about 90:10 to about 60:40; preferably from about 80:20 to about 70:30.

The continuous, or invert emulsion phase of the drilling fluid, or mud, of this invention is emulsified by dispersing therein at least one additive selected from the group consisting of weighting agents, emulsifiers, wetting agents, viscosifiers, fluid loss control agents, proppants for use in fracturing subterranean formations, and particulate agents as used in gravel packs.

In forming the drilling fluid, or mud, generally one or more of the weighting agents, emulsifiers, wetting agents, viscosifiers, fluid loss control agents, proppants, and particulate agents are mixed with the paraffinic solvent composition to form an emulsion in which the latter forms a continuous oil phase, or water-in-oil invert emulsion phase. In such systems, the high purity solvent composition constitutes generally from about 50 percent to about 95 percent, and more often and preferably, from about 60 percent to about 80 percent of the total drilling fluid, or mud, based on the total volume of the composition; with the balance of the drilling fluid, or mud, being water, brine or other additive, or additives. A drilling fluid, or mud, of this character provides excellent rheological properties under a wide variety of drilling conditions. Exemplary of additives useful in the practice of this invention are:

weighting materials such as barite, iron oxide, calcium oxide, etc.; emulsifiers such as fatty acids, soaps of fatty acids, and fatty acid derivatives such as amido-amines, polyamides, polyamines, esters, e.g., sorbitan monoleate polyethoxylate, etc.; wetting agents such as crude tall oil, organic phosphate esters, modified imidazolines and amido-amines, alkyl aromatic sulfates and sulfonates, etc.; viscosifiers such as organophilic clays, oil soluble polymers, polyamide resins, polycarboxylic acids and soaps, etc.; fluid loss control materials such as modified lignites, polymers, asphaltic compounds and the like, etc.; proppant materials such as sand grains, walnut shells, etc.; gravel and the like. Water, or brine, as suggested, can also be present in or added to the drilling fluid, or mud. Typically, the weighting agent is added in concentrations ranging up to about 18 pounds, per barrel of paraffinic solvent; the emulsifiers and wetting agents, respectively, in concentrations ranging from about 2 to about 6 pounds, per barrel of paraffinic solvent; the viscosifiers in concentrations ranging from about 1 to about 10 pounds per barrel of paraffinic solvent; and the fluid loss control agents in concentrations ranging from about 1 to about 20 pounds per barrel of paraffinic solvent.

#### 4. Detailed Description

The paraffinic oil base, or solvent, component for the drilling fluid, or mud, can be obtained from a Fischer-Tropsch reaction product or wax, or from slack waxes which serve as feeds for the production of the solvent component of the mud. The solvent component is produced by the hydrocracking and hydroisomerization of  $C_5+$  paraffinic, or waxy hydrocarbon feeds, especially Fischer-Tropsch waxes, or reaction products at least a fraction of which boils above  $700^{\circ}\text{F}$ , i.e., at  $700^{\circ}\text{F}+$ . The waxy feed is contacted, with hydrogen, over a dual functional catalyst to produce hydroisomerization and hydrocracking reactions sufficient to convert at least about 20 percent to about 90 percent, preferably from about 30 percent to about 80 percent, on a once through basis based on the weight of the  $700^{\circ}\text{F}+$  feed component, or  $700^{\circ}\text{F}+$  feed, to  $700^{\circ}\text{F}-$  materials, and produce a liquid product boiling at from about  $74^{\circ}\text{F}$  to about  $1050^{\circ}\text{F}$ , i.e., a  $C_5$ - $1050^{\circ}\text{F}$  liquid product, or crude fraction. The  $C_5$ - $1050^{\circ}\text{F}$  crude fraction is topped via atmospheric distillation to produce two fractions, (i) a

low boiling fraction having an initial boiling point ranging between about 74°F and about 100°F, and an upper end boiling point of about 700°F, and (ii) a high boiling fraction having an initial boiling point of about 700°F, and an upper end boiling point of about 1050°F, or higher, i.e., 1050°F+. The low boiling fraction (i), or fraction boiling between about C<sub>5</sub> and about 700°F, which is constituted substantially of paraffins, provides a material from which the solvent component of the drilling fluid or mud, can be recovered, or the solvent component for the drilling fluid, or mud, may be obtained from slack waxes. Slack waxes are the by-products of dewaxing operations where a diluent such as propane or a ketone (e.g., methylethyl ketone, methyl isobutyl ketone) or other diluent is employed to promote wax crystal growth, the wax being removed from the lubricating oil base stock by filtration or other suitable means. The slack waxes are generally paraffinic in nature, boil above about 600°F, preferably in the range of 600°F to about 1050°F, and may contain from about 1 to about 35 wt.% oil. Waxes with low oil contents, e.g., 5-20 wt.% are preferred; however, waxy distillates or raffinates containing 5-45% wax may also be used as feeds. Slack waxes are usually freed of polynuclear aromatics and hetero-atom compounds by techniques known in the art; e.g., mild hydrotreating as described in U.S. Patent No. 4,900,707, which also reduces sulfur and nitrogen levels preferably to less than 5 ppm and less than 2 ppm, respectively. Fischer-Tropsch waxes are preferred feed materials, having negligible amounts of aromatics, sulfur and nitrogen compounds. The Fischer-Tropsch liquid, and wax, is characterized as the product of a Fischer-Tropsch process wherein a synthetic gas, or mixture of hydrogen and carbon monoxide, is processed at elevated temperature over a supported catalyst comprised of a Group VIII metal, or metals, of the Periodic Table of The Elements (Sargent-Welch Scientific Company, Copyright 1968), e.g., cobalt, ruthenium, iron, etc.

The Fischer-Tropsch liquid contains C<sub>5</sub>+, preferably C<sub>10</sub>+, more preferably C<sub>20</sub>+ paraffins. A distillation showing the fractional make up (±10 wt.% for each fraction) of a typical Fischer-Tropsch product is as follows:

<u>Boiling Temperature Range</u>	<u>Wt. % of Fraction</u>
IBP - 320°F	13
320 - 500°F	23
500 - 700°F	19
700 - 1050°F	34
1050°F+	<u>11</u>
	100

A 700°F+ wax feed, or wax feed containing 700°F+ hydrocarbons, preferably the former, is contacted, with hydrogen, at hydrocracking/hydroisomerization conditions over a bifunctional catalyst, or catalyst containing a metal, or metals, hydrogenation component and an acidic oxide support component active in producing both hydrocracking and hydroisomerization reactions. Preferably, a fixed bed of the catalyst is contacted with the feed at conditions which convert about 20 to 90 wt.%, preferably about 30 to 80 wt.% of the 700°F+ feed (or 700°F+ component of the feed) to a low boiling fraction having an initial boiling point of about C<sub>5</sub> (about 74°F to about 100°F) and an end boiling point of about 700°F, and a higher boiling fraction having an initial boiling point corresponding to the upper end boiling point of the low boiling fraction and a higher end boiling point of 1050°F, or greater. In general, the hydrocracking/hydroisomerization reaction is conducted by contacting the waxy feed over the catalyst at a controlled combination of conditions which produce these levels of conversion, e.g., by selection of temperatures ranging from about 400°F to about 850°F, preferably from about 500°F to about 700°F, pressures ranging generally from about 100 pounds per square inch gauge (psig) to about 1500 psig, preferably from about 300 psig to about 1000 psig, hydrogen treat gas rates ranging from about 1000 SCFB to about 10,000 SCFB, preferably from about 2000 SCFB to about 5000 SCFB, and space velocities ranging generally from about 0.5 LHSV to about 10 LHSV, preferably from about 0.5 LHSV to about 2 LHSV. Optionally, and preferably, after the hydrocracking/hydroisomerization step is completed, the high purity solvent composition that is recovered, and which is to be used as a component of the drilling fluid, or mud, is subjected to a mild hydrotreating step to ensure that the finished product is free of aromatics.



The active metal component of the catalyst used in the hydrocracking/hydroisomerization reaction is preferably a Group VIII metal, or metals, of the Periodic Table Of The Elements (Sargent-Welch Scientific Company Copyright 1968) in amount sufficient to be catalytically active for hydrocracking and hydroisomerization of the waxy feed. The catalyst may also contain, in addition to the Group VIII metal, or metals, a Group IB and/or a Group VIB metal, or metals, of the Periodic Table. Generally, metal concentrations range from about 0.05 percent to about 20 percent, based on the total weight of the catalyst (wt.%), preferably from about 0.1 wt. percent to about 10 wt. percent. Exemplary of such metals are the non-noble Group VIII metals such as nickel and cobalt, or mixtures of these metals with each other or with other metals, such as copper, a Group IB metal, or molybdenum, a Group VIB metal. Palladium and platinum are exemplary of suitable Group VIII noble metals. The metal, or metals, is incorporated with the support component of the catalyst by known methods, e.g., by impregnation of the support with a solution of a suitable salt or acid of the metal, or metals, drying and calcination.

The catalyst support is constituted of metal oxide, or metal oxides, components at least one component of which is an acidic oxide active in producing olefin cracking and hydroisomerization reactions. Exemplary oxides include silica, silica-alumina, clays, e.g., pillared clays, magnesia, titania, zirconia, halides, e.g., chlorided alumina, and the like. The catalyst support is preferably constituted of silica and alumina, a particularly preferred support being constituted of up to about 35 wt.% silica, preferably from about 2 wt.% to about 35 wt.% silica, and having the following porestructural characteristics:

<u>Pore Radius, Å</u>	<u>Pore Volume</u>
0-300	>0.03 ml/g
100-75,000	<0.35 ml/g
0-30	<25% of the volume of the pores with 0-300 Å radius
100-300	<40% of the volume of the pores with 0-300 Å radius

The base silica and alumina materials can be, e.g., soluble silica containing compounds such as alkali metal silicates (preferably where  $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2$  to  $1:4$ ), tetraalkoxy silane, orthosilic acid ester, etc.; sulfates, nitrates, or chlorides of aluminum alkali metal aluminates; or inorganic or organic salts of alkoxides or the like. When precipitating the hydrates of silica or alumina from a solution of such starting materials, a suitable acid or base is added and the pH is set within a range of about 6.0 to 11.0. Precipitation and aging are carried out, with heating, by adding an acid or base under reflux to prevent evaporation of the treating liquid and change of pH. The remainder of the support producing process is the same as those commonly employed, including filtering, drying and calcination of the support material.

The support may also contain small amounts, e.g., 1-30 wt.%, of materials such as magnesia, titania, zirconia, hafnia, or the like.

Support materials and their preparation are described more fully in U.S. Patent No. 3,843,509 incorporated herein by reference. The support materials generally have a surface area ranging from about 180-400  $\text{m}^2/\text{g}$ , preferably 230-375  $\text{m}^2/\text{g}$ , a pore volume generally of about 0.3 to 1.0  $\text{ml/g}$ , preferably about 0.5 to 0.95  $\text{ml/g}$ , bulk density of generally about 0.5-1.0  $\text{g/ml}$ , and a side crushing strength of about 0.8 to 3.5  $\text{kg/mm}$ .

The following examples are illustrative of the more salient features of this invention. All parts, and percentages, are given in terms of weight unless otherwise specified.

#### Examples

a) A mixture of hydrogen and carbon monoxide synthesis gas ( $\text{H}_2:\text{CO}$  2.11-2.16) was converted to heavy paraffins in a slurry Fischer-Tropsch reactor. A titania supported cobalt rhenium catalyst was utilized for the Fischer-Tropsch reaction. The reaction was conducted at 422-428°F, 287-289 psig, and the feed was introduced at a linear velocity of 12 to 17.5  $\text{cm/sec}$ . The alpha of the Fischer-Tropsch synthesis step was 0.92. The paraffinic

Fischer-Tropsch product was isolated in three nominally different boiling streams; separated by utilizing a rough flash. The three boiling fractions which were obtained were: 1) a C<sub>5</sub>-500°F boiling fraction, i.e., F-T cold separator liquids; 2) a 500-700°F boiling fraction, i.e., F-T hot separator liquids; and 3) a 700°F+ boiling fraction, i.e., an F-T reactor wax.

b) The 700°F+ boiling fraction, or F-T reactor wax, having a boiling point distribution as follows: IBP-500°F, 1.0%, 500°F-700°F, 28.1%, and 700°F+, 70.9%, was then hydroisomerized and hydrocracked over a dual functional catalyst consisting of cobalt (CoO, 3.2 wt%) and molybdenum (MoO<sub>3</sub>, 15.2 wt%) on a silica-alumina cogel acidic support, 15.5 wt% of which is SiO<sub>2</sub>. The catalyst had a surface area of 266 m<sup>2</sup>/g and pore volume (PV<sub>H<sub>2</sub>O</sub>) of 0.64 ml/g. The conditions for the reaction are listed in Table 1 and were sufficient to provide approximately 50% 700°F+ conversion where 700°F+ conversion is defined as:

$$700^{\circ}\text{F}+ \text{Conv.} = [1 - (\text{wt}\% \text{ 700}^{\circ}\text{F}+ \text{ in product})/(\text{wt}\% \text{ 700}^{\circ}\text{F}+ \text{ in feed})] \times 100$$

Table 1

Operating Conditions

Temp., °F	690
LHSV, v/v/h	0.6 - 0.7
H <sub>2</sub> Pressure, psig (pure)	725
H <sub>2</sub> Treat rate, SCF/B	2500

c) The reaction product, or hydroisomerate, was then fractionated in a 15/5 distillation to yield a 500-700°F fraction. This fraction was then mildly hydrotreated over a commercial massive nickel on alumina catalyst to remove trace levels of aromatics. The conditions for this reaction are given in Table 2. The aromatic content of the 500-700°F feedstock was determined using a UV/Vis absorbance technique. According to this test, the aromatic content of the feedstock was 0.078 mol/l which equates to approximately 0.80 wt% aromatics as benzene. The aromatic reduction from the hydrotreating step was approximately 99% with essentially no boiling point conversion.

Table 2

## Hydrotreating Reaction Conditions

Temperature, °F	400
H <sub>2</sub> Pressure, psig (pure)	400
H <sub>2</sub> Treat Gas Rate, SCF/B	3500
LHSV, v/v/h	1.0
Aromatic Conversion, wt%	≈99

d) The hydrotreated product was then fractionated using a 15/5 distillation into a IBP-550°F fraction and a 550°F+ fraction. The properties of each fraction as well as a commercially available synthetic oil, NOVASOL, and two mineral oil samples, ESCAID 110 and ESCAID 240, are compared in Table 3. NOVASOL is a synthetic polyalphaolefin marketed by M-I Drilling Fluid Company in synthetic base muds, SBMs. ESCAID 110 and ESCAID 240 are mineral oils marketed by Exxon for use in oil base muds, OBMs.

Table 3

## Base Oil Properties

	ESCAID 110	ESCAID 240	NOVASOL	IBP-550°F	550°F+
Distillation, IBP, °F	408	476	590	178	553
Distillation, FBP, °F	455	513		596	771
Flash Point, °F	176	234	275-311	225	
Kinematic Viscosity, cSt @ 100°F	1.7	2.7		2.57	4.51
Kinematic Viscosity, cSt @ 120°F	1.6			1.76	2.85
Kinematic Viscosity, cSt @ 212°F	0.8		1.8-2.0		1.58
Pour Point, °F	-42	-9	<-85	-15	
Specific Gravity	.798	0.816	0.79-0.82	0.778	
Aromatic Content, wt%	<0.2	<0.5	"None"	0.05	0.03

e) The hydrotreated IBP-550°F, characterized in Table 3, along with ESCAID 110 and NOVASOL were formulated into finished drilling muds with a density of about 13 lb/gal and an oil:water ratio of 70:30. The formulations of the three drilling fluids as well as basic drilling mud test results are summarized in Table 4. All muds were prepared according to the order recommended by M-I Drilling Fluids. All testing was in accordance with API RP-13B-2 (Second Edition, Dec. 1, 1991) "Standard Procedure for Field Testing Oil - Base Drilling Fluids". The viscosity of IBP-550°F sample at both high and low shear rates is very similar to that of both the NOVASOL and ESCAID 110 drilling fluids (Viscosity, cP vs. Shear Rate, 1/sec). The fluid loss at 100 psi and 300°F is comparable for all three base oils. However, at 500 psi and 300°F all three samples passed an emulsion rather than water-free, clear oil filtrates as would normally be required. It should be noted, however, that the M-I formulation instructions did not specify the addition of a separate fluid loss additive. Further testing showed that none of the muds tested caused a sheen when following the EPA Static Sheen test protocol. These results show that drilling fluids of excellent performance can be prepared using these base oils.

Table 4

## Composition of Drilling Fluids

<u>Oil Phase</u>	<u>NOVASOL</u>	<u>ESCAID 110</u>	<u>IBP-550°F</u>
Base Oil, bbl	0.56	0.56	0.56
Base Oil, mL/bbl	196	196	196
Bentone 38, lb/bbl	2	8	5
Lime, lb/bbl	6	6	6
Novamud, lb/bbl	6	6	6
30% CaCl <sub>2</sub> (10.8) bbl	0.21	0.21	0.21
30% CaCl <sub>2</sub> , mL/bbl	174	174	174
Barite, lb/bbl	278	278	278
NOVAMUD, lb/bbl	1	1	1
Mud Weight, lb/gal	13.2	13.1	13.2
Gel, 10", 10', lb/100 ft <sup>2</sup>	11/17	16/28	11/20
Apparent Viscosity, cP	35	33	29
Plastic Viscosity, cP	23	19	24
Yield Point, lb/100 ft <sup>2</sup>	23	19	10
E.S. 23C, Volts	620	600	640
API Fluid Loss, mL	.03	1.2	0.6
HT/HP Fluid Loss @ 300°F, mL	4.2 (emul)	2.6 (emul)	2.4 (emul)

f) The three drilling fluids were then analyzed to determine the acute toxicity of the samples to mysid shrimp (*Mysidopsis bahia*). The testing procedure used were those required by the U.S. Environmental Protection Agency to determine compliance with toxicity limitations in NPDES discharge permits for offshore oil and gas operations (EPA, 1985, 1993).

A preliminary range-finding test was conducted to determine appropriate concentrations to be tested during the definitive test. For the range-finding test, there were

10 mysids per replicate and one replicate per concentration. The concentrations for the range-finding test were: control; 30,000; 60,000; 125,000; 250,000; 500,000; and 1,000,000 ppm suspended particulate phase. Survival of mysids in the drilling fluid and copper sulfate test solutions were analyzed and interpreted using standard techniques (Finney, 1971; Stephan, 1977). If there was any control mortality in the definitive test a maximum likelihood estimation procedure with adjustments for natural responsiveness (Finney, 1971) was used to adjust the  $LC_{50}$  for the natural mortality observed. The Spearman-Kärber computer program was used to analyze the data to compute  $LC_{50}$ 's (i.e., the concentration lethal to 50% of the test organisms) and 95% confidence intervals.

The results derived from the range-finding test, the definitive test and the standard toxicant (copper sulfate) test are shown in Table 5. Mortality in the seawater control was 0% for the tests performed on the ESCAID-110 and IBP-550°F fluids and 5% for the test performed on the NOVASOL sample. The response of a subsample of the mysid population used in this toxicity test to a reference toxicant (copper sulfate), as well as the survival in the seawater controls, showed that the test organisms were in suitable condition for use in toxicity testing. As expected the drilling fluids formulated with the NOVASOL and the ESCAID 110 base oils performed quite well in the toxicity testing. However, the base oil IBP-550°F, was an order of magnitude less toxic.

It is apparent that various modifications and changes can be made without departing the spirit and scope of the invention.



Table 5

Results from Mysid Shrimp (*Mysidopsis bahia*) Acute Toxicity Test

Test	NOVASOL Drilling Fluid	ESCAID 110 Drilling Fluid	IBP-500°F Drilling Fluid
Range-Finder			
LC <sub>50</sub> , ppm SSP	125,000-250,000	0-30,000	125,000-250,000
95% Confidence Limits, ppm	NA	NA	NA
Definitive			
LC <sub>50</sub> , ppm SSP	16,266	19,882	192,500
95% Confidence Limits, ppm	6.5 x 10 <sup>-7</sup> - 50,483	16,683-23,972	173,900-213,100
Standard Toxicant			
LC <sub>50</sub> , µg/L Cu	243	243	243
95% Confidence Limits, µg/L	150-300	150-300	150-300
Mortality in Seawater	5.0%	0%	0%

## CLAIMS:

1. A substantially non-toxic, non-polluting, biodegradable drilling fluid composition useful in the production of oil and gas having a continuous oil phase which comprises a mixture of  $C_{10}$ - $C_{24}$  n-paraffins and isoparaffins having an isoparaffin:n-paraffin molar ratio ranging from about 0.5:1 to about 9:1, and the isoparaffins of the mixture contains greater than 50 percent of mono-methyl species, based on the total weight of the isoparaffins in the mixture.
2. The composition of Claim 1 wherein the mixture of paraffins has a carbon number ranging from about  $C_{12}$  to about  $C_{18}$ .
3. The composition of Claim 1 wherein the mixture contains greater than 70 percent of the mono-methyl species.
4. The composition of Claim 1 wherein the mixture boils at a temperature ranging from about 320°F to about 700°F.
5. The composition of Claim 4 wherein the mixture boils within a range of from about 500°F to about 700°F.
6. The composition of Claim 1 wherein the mixture is of carbon number ranging from about  $C_{12}$ - $C_{18}$ , the mixture contains greater than 70 percent of the mono-methyl species and boils within a range of from about 500°F to about 700°F.
7. The composition of Claim 1 wherein the paraffinic mixture has a molar ratio of isoparaffins:n-paraffins ranging from about 1:1 to about 4:1.
8. The composition of any of Claims 1 through 7 wherein the mixture further includes at least one additive selected from the group consisting of weighting agents, emulsifiers, wetting agents, viscosifiers, fluid loss control agents, proppants and particulate agents.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/04611

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 97 21787 A (EXXON RESEARCH) 19 June 1997 cited in the application see the whole document	1-7
Y,P	US 5 569 642 A (K.F.LIN) 29 October 1996 see column 1, line 62 - column 2, line 10 see column 2, line 40 - column 3, line 43; claims 1-8	1-3,8
Y	US 5 096 883 A (J.D.MERCER) 17 March 1992 see column 2, line 39 - line 68 see column 3, line 35 - column 4, line 44	1-3,8
Y	WO 95 09215 A (MOBIL OIL CORPORATION) 6 April 1995 see page 3, line 13 - page 5, line 25 see page 8, line 1 - line 24; claims 1-19	1,2,8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*A\* document member of the same patent family

Date of the actual completion of the international search

8 August 1997

Date of mailing of the international search report

14.08.97

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/04611

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95 06694 A (SCHLUMBERGER) 9 March 1995 see page 2, line 21 - page 3, line 34 see page 5, line 22 - line 29 see example 4	1,2,8
Y	GB 2 117 429 A (MILCHEM INC.) 12 October 1983 see page 2, line 54 - page 3, line 58	1,2,8

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Invention application No

PCT/US 97/04611

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9721787 A	19-06-97	NONE	
US 5569642 A	29-10-96	NONE	
US 5096883 A	17-03-92	NONE	
WO 9509215 A	06-04-95	US 5498596 A	12-03-96
		AU 1664095 A	18-04-95
		EP 0690899 A	10-01-96
		JP 9503017 T	25-03-97
		NO 951553 A	24-04-95
WO 9506694 A	09-03-95	AU 7504394 A	22-03-95
		CN 1114110 A	27-12-95
		EP 0667890 A	23-08-95
		GB 2287052 A,B	06-09-95
		NO 951638 A	28-06-95
GB 2117429 A	12-10-83	AU 1166583 A	25-08-83
		FR 2521584 A	19-08-83
		WO 8302951 A	01-09-83
		NL 8300608 A	16-09-83
		AU 1166483 A	25-08-83
		AU 1166683 A	25-08-83
		FR 2521582 A	19-08-83
		FR 2521583 A	19-08-83
		WO 8302949 A	01-09-83
		WO 8302950 A	01-09-83
		GB 2115458 A	07-09-83
		GB 2115459 A	07-09-83
		NL 8300607 A	16-09-83
		NL 8300609 A	16-09-83

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